ONE-STEP SYNTHESIS OF ADN FROM FOX-12

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ABSTRACT

Ammonium dinitramide (ADN) is currently under investigation as a replacement for ammonium perchlorate, both for environmental and toxicological reasons. Another promising application is ADN-based liquid monopropellants as a replacement for hydrazine, which is highly toxic and carcinogenic.

Production of ADN is today normally performed via guanylurea dinitramide (FOX-12, GUDN) by reaction with potassium hydroxide to yield potassium dinitramide (KDN). In a second reaction step, KDN is reacted with ammonium sulphate to give ADN. In our new improved process, ADN is synthesized from FOX-12 in one single reaction step. In the reaction between FOX-12 and a source of ammonium, for example ammonium sulphate, the exchange of cations between the two reactants is possible and ADN can be isolated.

This straight-forward approach looks simple and seems as the most obvious way of producing ADN from FOX-12. However, this reaction is more complex than it first appears and has hitherto, neither been reported, nor used in the production of ADN.

The simplified process improves purity, reduces the amount of by-products and allows production of ADN at a potentially lower cost, which is crucial to favour the use of ADN.

KEY WORD: *Ammonium sulphate, Ammonium dinitramide, Potassium dinitramide, Guanylurea sulphate, Guanylurea dinitramide.*

INTRODUCTION

Current solid composite propellants are based on the oxidizer ammonium perchlorate (AP). AP has many desirable properties such as high oxygen content, high density, low explosive hazard and good

combustion properties. However, AP has a negative impact on the environment and on personal health [1-3] and generate vast amount of smoke [4]. Development of green solid propellants is currently ongoing in the EU project GRAIL (www.grail-h2020.eu), which has been granted to determine if it is feasible to replace AP with the green oxidizer ammonium dinitramide, ADN.

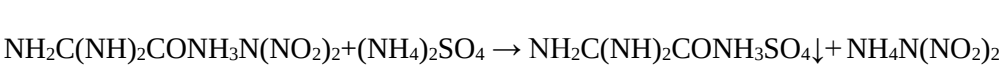
ADN can also be used in liquid monopropellants dissolved in fuel water mixtures. This type of liquid monopropellant is currently considered the most mature propellant to replace the toxic and carcinogenic monopropellant hydrazine [5]. ADN based liquid monopropellants and associated hardware are currently under development in the EU project Rheform (www.rheform-h2020.eu). For both these applications, ADN at lower cost is desired.

There are different approaches to synthesise ADN [6]. In one of the early methods the most powerful nitration agents, such as nitronium tetraflouroborate or dinitrogen pentoxide, was used to nitrate urethanes [7]. Other methods use direct nitration of ammonia with dinitrogen pentoxide to form ADN. Drawbacks with these methods are the high costs of the rare chemicals in large scale production.

Production of ADN is today normally performed by nitration of potassium or ammonium sulfaminate in mixed acids to dinitramidic acid, which is isolated as its guanylureonium salt *guanylurea dinitramide* (FOX-12). The latter is then converted using potassium hydroxide to yield *potassium dinitramide* (KDN) [8, 9]. In a final reaction step, KDN is reacted with ammonium sulphate to give ADN.

The drawback of the current production method is the two-step ion exchange reaction with the intermediate KDN. Apart from being more complex, the presence of potassium impurities in the final product might increase the radar signature [10]. For liquid ADN based propellants potassium might also cause problems such as catalyst poisoning [11].

As FOX-12 is converted first into KDN and finally ADN in two ion exchange reactions, it should theoretically be possible to convert FOX-12 into ADN in one reaction step *(Scheme 1).*



Scheme 1 Synthesis of ammonium dinitramide from FOX-12

An ion exchange between a source of ammonium – for example ammonium sulphate – should, under the right conditions, yield ADN from FOX-12 and the by-product guanylurea sulphate in a one-step reaction. This would eliminate presence of potassium and reduce the number of reactions steps to one.

RESULTS

Ion exchange reaction between FOX-12 and ammonium sulphate were performed in different amounts of water. FOX-12 is, unlike most dinitramide salts, non-hygroscopic and poorly soluble in water [12, 13]. The solubility of FOX-12 in water is estimated to be 10 weight% at 100 °C, and 0.1 % at room temperature. To ensure dissolution of FOX-12 and ammonium sulphate, initial synthesis were performed using large amounts of water.

The reactions were performed using the parameters shown in Table 1 *and by the following general procedure. FOX-12 (10 g, 47.8 mmol) and ammonium sulphate (7.58 g, 57.4 mmol) was added in water. The resulting suspension was heated until a homogeneous solution was obtained. This was then poured into 2-propanol. The formed precipitation was filtered off. The filtrate was concentrated under reduced pressure. To the resulting residue 2-propanol (100 ml) was added and the undissolved solid was filtered off. The filtrate was concentrated under reduced pressure to yield ammonium dinitramide (ADN). The amount of ADN formed was determined by the weight of the isolated material. The results are shown in* Table 1 *and* Figure 1.

Table 1 ADN yields at different volumes of water.

Water (ml)	**Ethanol (ml)**	**FOX-12 (g)**	**$(NH_4)_2SO_4$ (eq)**	**Quenched in 2-popanol (ml)**	**Yield (%)**
0	100	10	1.2	0	3.5
30	0	10	1.2	300	42.9
75	0	10	1.2	750	60.6
100	0	10	1.2	1000	67.9
125	0	10	1.2	1250	75.8
150	0	10	1.2	1500	83.6
200	0	10	1.2	2000	82.9

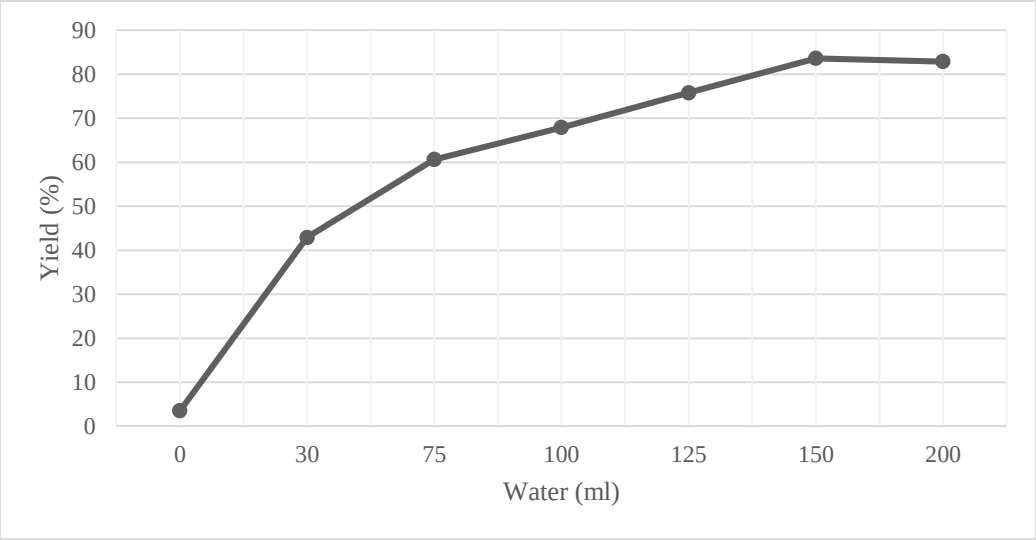


Figure 1 ADN yields at different volumes of water

LCMS (Waters Xevo TQ-S, Acquity UPLC), using unpublished method by E. Holmgren FOI [14], displayed synthetized product without presence of potassium, guanylurea, sulphate or nitrate (*Figure 2*, *Figure 3*).

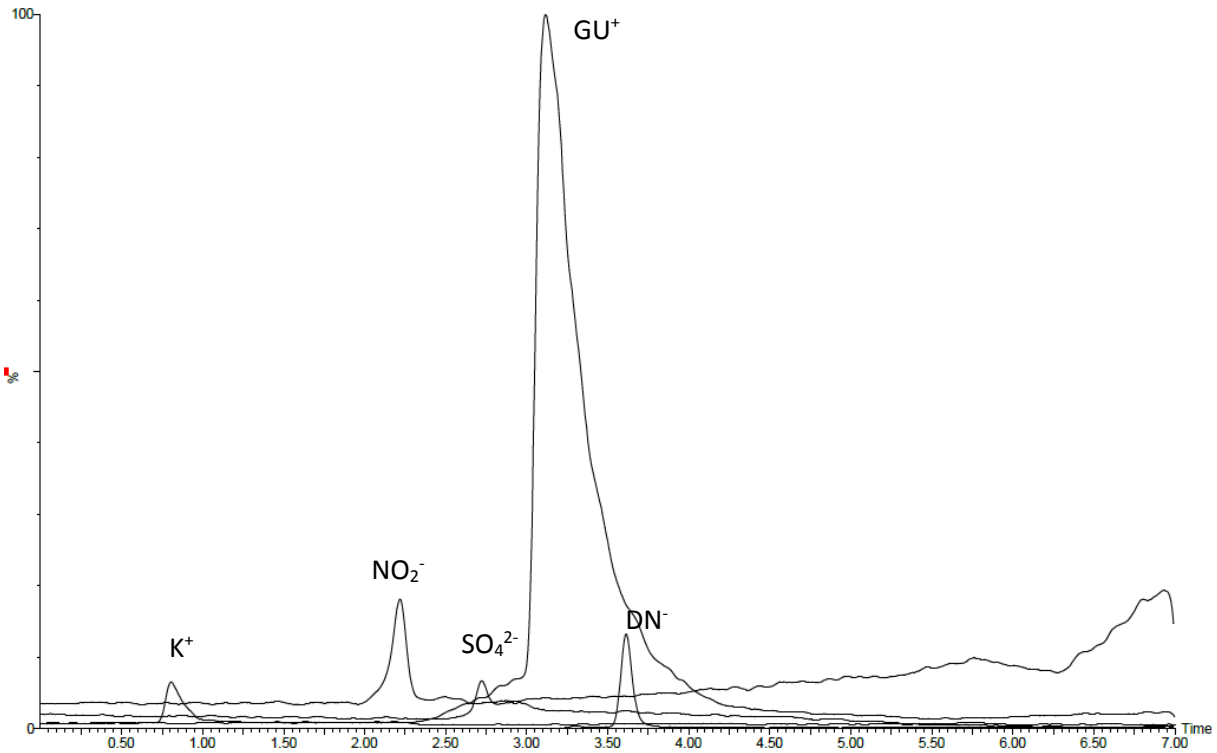


Figure 2 LCMS,[14]. Reference sample. K^+ potassium, NO_2^- nitrate, SO_4^{2-} sulphate, GU^+ guanylureonium, and DN^- dinitramide ions

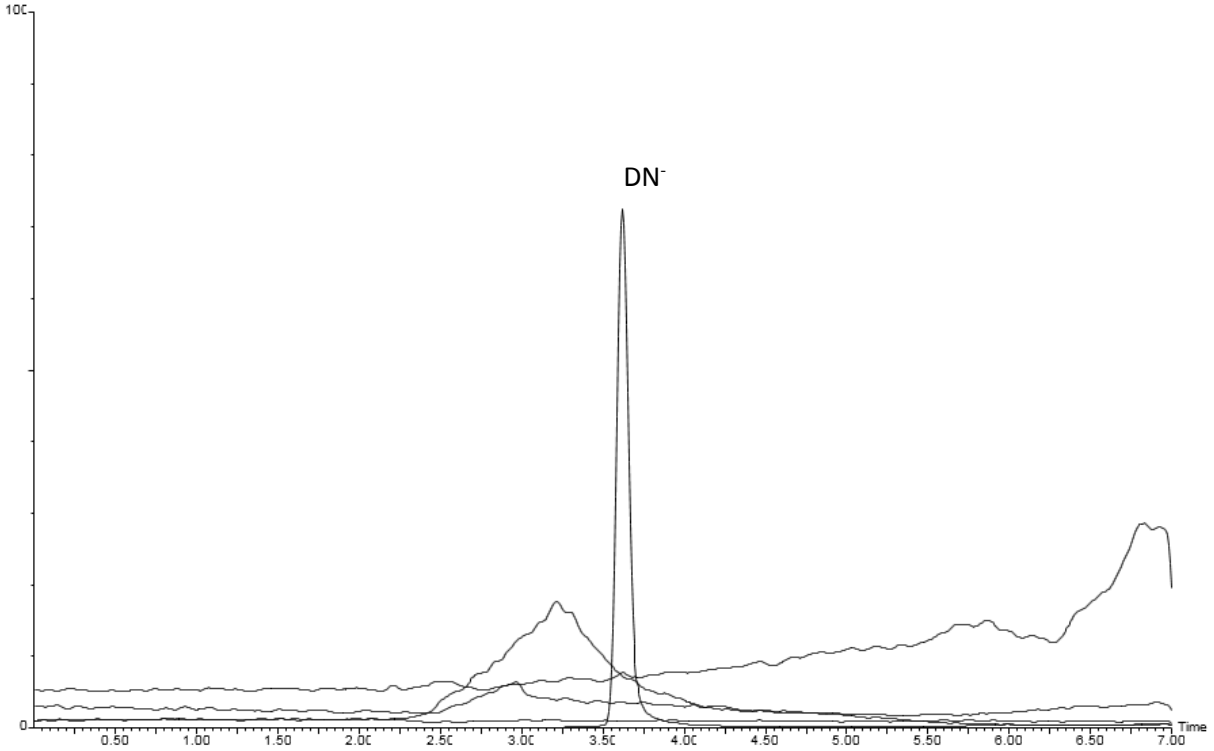


Figure 3 LCMS [14]. Synthesized product. Dinitramide ion. Everything else in the chromatogram besides the dinitramide ion is background noise.

DISCUSSION

The ion exchange reaction between FOX-12 and ammonium sulphate can take place thanks to the difference in solubility of the different reaction components. When studying the different components, one can see that guanylurea sulphate is not very soluble in most solutions having a low water content. Ammonium sulphate in the same solutions displays higher solubility.

FOX-12 is poorly soluble in water. However, the introduction of ammonium sulphate into the reaction mixture made the solid FOX-12 disappear, which indicated a reaction between the two.

Combining the above information, FOX-12 can undergo ion exchange reaction in the presence of ammonium sulphate and a water and/or water/alcohol solution. Precipitation of guanylurea sulphate in the reaction mixture drives the reaction to favour the desired product, ADN.

By reducing the amount of water, the yield decreased linearly. The opposite was also observed. By increasing the amount of water, the yield increased linearly, but only up to the point of 80% yield. After this point, increasing water content did not affect the yield.

At first it was difficult to explain how the amount of water could affect the yield, especially when higher amounts of water increased the yield of ADN. It is also difficult to explain why this reaction would not yield 100%, as the reaction parameters should favour total conversion.

By LC-MS analyses it was shown that the first precipitation only contained guanylurea sulphate and ammonium sulphate.

Pure FOX-12 was collected in the second precipitation. Even higher amounts of ammonium sulphate in the reaction mixture did not affect the yield. The missing percentage from quantitative yield was retrieved as FOX-12 in filtration step two. Why this material is inert in the reaction mixture is unknown. The reason might be some sort of co-ordination between water and FOX-12 which makes the material inert and prevents it from undergoing the ion exchange reaction with ammonium sulphate.

By heating the reaction mixture and quenching the resulting solution into cold 2-propanol, the yield of ADN increased. This could indicate that hydrogen bonds interfered with the ion exchange reaction, as the hydrogen bonds weaken at higher temperature.

One very important factor in this reaction is that ADN is not the favoured product if guanylurea and ammonium are competing to form stable compound with dinitramide. This is the case in protic solvents, such as water. By control of the polarity of the reaction solution, by altering the amount of alcohol/water, ammonium sulphate can still be soluble, whereas guanylurea sulphate is not, then ADN stays in solution and is the favoured product.

CONSLUSIONS

We have shown that this simplified process improves purity, reduces the amount of by-products and allows production of ADN potentially at a lower cost. This process also eliminates presence of potassium and reduce the number of reactions steps to one. The crucial step to reduce the production cost of ADN, using this new process, is to reduce the amount of water in the reaction. Current investigation of different solvents and/or mixtures of solvents in this ion exchange reaction are ongoing and the results are very promising.

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